KFA

KERNFORSCHUNGSANLAGE JÜLICH GmbH

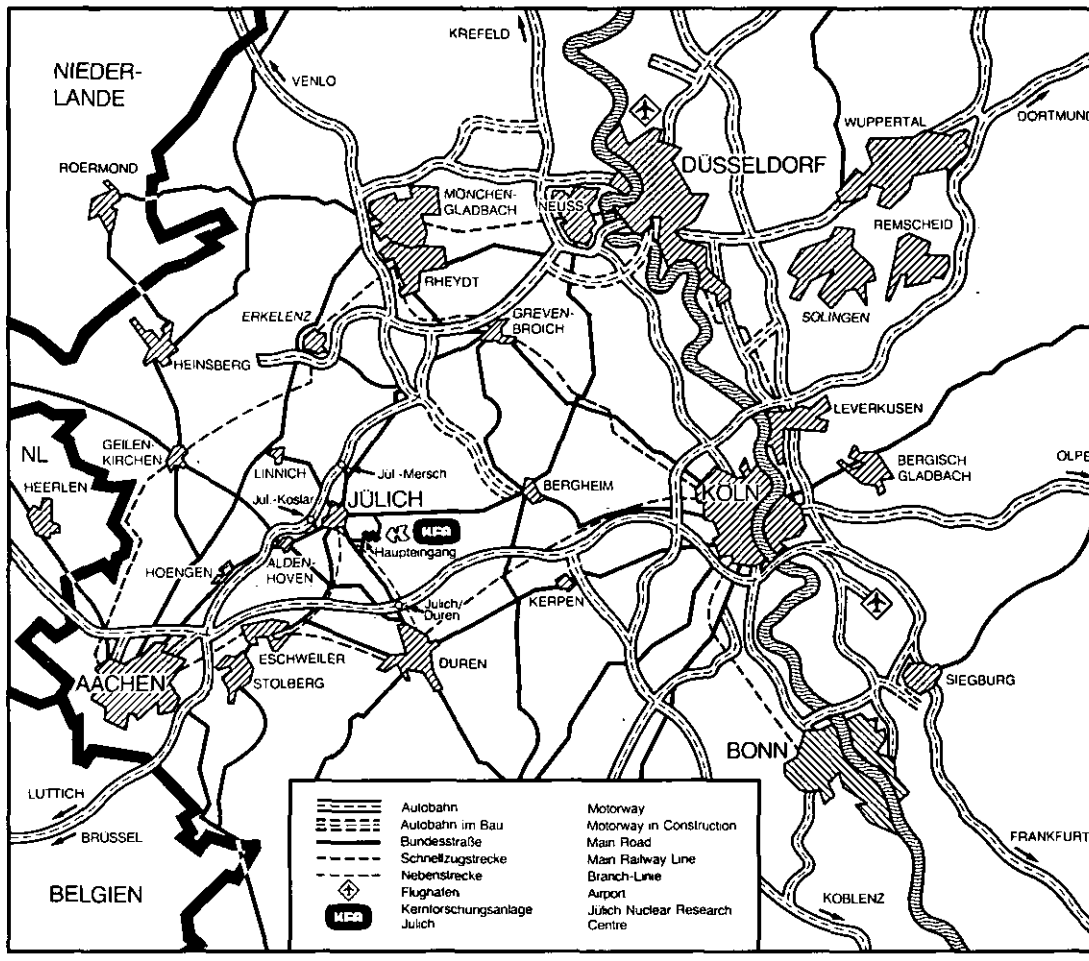
CONTRIBUTIONS FOR THE SEVENTEENTH BIENNIAL CONFERENCE ON CARBON

Papers to be read at the Conference
in the University of Kentucky
Lexington, Kentucky

June 16-21, 1985

compiled by
W. Delle

Jül-Conf-52
June 1985
ISSN 0344-5798



Als Manuskript gedruckt

Berichte der Kernforschungsanlage Jülich – Jül-Conf-Nr. 52

Zu beziehen durch: ZENTRALBIBLIOTHEK der Kernforschungsanlage Jülich GmbH
Postfach 1913 · D-5170 Jülich (Bundesrepublik Deutschland)
Telefon: 02461/610 · Telex: 833556-0 kf d

CONTRIBUTIONS FOR THE SEVENTEENTH BIENNIAL CONFERENCE ON CARBON

compiled by
W. Delle

List of contributors:
L. Binkele, W.Delle, G. Haag, G. Heit*, N. Kirch, H. Nickel, H.A. Schulze, R.-E. Schulze, W.F. Sommer**, K.H. Victor***, E. Ziermann****

* NUKEM/HOBEG Company, D-6450 Hanau, Federal Republic of Germany
** Los Alamos National Laboratory, H 383 MP-13, Los Alamos, NM 87545, USA
*** Fa. Pacific Wietz GmbH u. Co. KG, D-4600 Dortmund 72, Federal Republic of Germany
**** Arbeitsgemeinschaft Versuchsreaktor GmbH, Stetternicher Forst, D-5170 Jülich, Federal Republic of Germany

Kernforschungs-
anlage Jülich
GmbH IRW

Jül-Conf-52

Juni 1985

BEITRÄGE ZUR
17th BIENNIAL CONFERENCE ON CARBON
VOM 16. - 21. Juni 1985

ZUSAMMENGESTELLT VON
W. DELLE

KURZFASSUNG

Dieser Bericht enthält die Zusammenstellung von Beiträgen für die 17th Biennal Conference on Carbon, an der Mitarbeit der KFA Jülich GmbH maßgeblich beteiligt waren. In den Beiträgen werden Ergebnisse dargestellt, die auf den Gebieten der Verwendung des Kohlenstoffes bei der in der Bundesrepublik Deutschland geplanten Spallations-Neutronenquelle und im Hochtemperaturreaktor erzielt wurden.

CONTRIBUTIONS FOR THE
17th BIENNIAL CONFERENCE ON CARBON
June 16-21, 1985

COMPILED BY
W. DELLE

ABSTRACT

This report is the compilation of the papers prepared by KFA Jülich GmbH for the 17th Biennial Conference on Carbon. In the contributions, results are presented which were obtained from the application of carbon in the High Temperature Gas-Cooled Reactor and for the Spallation Neutron Source planned in the Federal Republic of Germany.

Contents

1. Einleitung

In den USA finden jeweils im Abstand von zwei Jahren Kohlenstoff-Konferenzen statt, auf denen Wissenschaftler und Techniker aus aller Welt ihre neuesten Forschungs- und Entwicklungsarbeiten vorstellen und diskutieren können. Die Konferenz wird von der American Carbon Society und der Institution, an der die Konferenz jeweils stattfindet, getragen. Im Jahre 1985 wird dies die University of Kentucky in Lexington sein.

In den Jahren zwischen diesen Konferenzen finden entsprechende Veranstaltungen in Europa statt. Im Jahre 1982 wurden in London die Sixth London International Conference on Carbon and Graphite CARBON '82 und im Jahre 1984 in Bordeaux die International Carbon Conference CARBONE 84 abgehalten. Von beiden Konferenzen gibt es KFA-Berichte über die Beiträge der KFA (JOL-Conf-47 und JOL-Conf-49). Die CARBON '86 wird 1986 vom Arbeitskreis Kohlenstoff der Deutschen Keramischen Gesellschaft in Baden-Baden ausgerichtet.

Auf der diesjährigen Konferenz in den Vereinigten Staaten werden Vorträge über folgende Gebiete gehalten:

- Intercalationswissenschaft
- elektronische Eigenschaften von Kohlenstoff- und Graphitsystemen
- Karbonisation und Graphitierung
- Oberflächenwissenschaften
- Reaktivität und Oxidation
- mechanische und thermische Eigenschaften
- Fasern und Verbundkörper
- Charakterisierung und Struktur
- Industrielle Anwendungen
- Nukleare Anwendungen.

Die im vorliegenden Bericht zusammengestellten Beiträge der KFA Jülich GmbH gehören zu dem zuletzt aufgeführten Bereich.

MATERIALS FOR SLIDING RING SEALS OF THE GERMAN SPALLATION NEUTRON SOURCE

R.-E. Schulze*, W. Delle*, H. Nickel*, H.A. Schulze*,
W.F. Sommer**, K.H. Victor***

* Kernforschungsanlage Jülich GmbH, Postfach 1913, D-5170 Jülich
** Los Alamos National Laboratory, H 383 MP-13, Los Alamos, NM 87545, USA
*** Fa. Pacific Wieth GmbH u. Co. KG, Flaspoete 101, D-4600 Dortmund 72

Introduction

The use of sliding ring seals in pump systems of nuclear power stations as well as in the target support and drive unit of the planned German Spallation Neutron Source (SNQ) (1) require suitable ring material combinations. Several combinations have been proposed for the ceramic rings of the two SNQ sliding seals (Tab. 1). They correspond to the types of seal, which particularly differ from each other by the kinds of friction:

- type I with mixed (solid/liquid) friction for sealing of the cooling water from the internal vacuum space
- type II with technical dry (solid/solid) friction for retention of water vapour, which might develop at the first seal, from the external vacuum space. (2)

The selection of promising candidates is based on industrial experience with conventional sliding ring seals as well as on results of seal tests, successfully performed in standard equipment at Pacific company. Futhermore, materials are included that are used in the pump systems of nuclear power stations.

Materials programme and investigations

The materials programme resulting from the selected combinations considers three categories of materials:

1. reaction-bonded silicon carbides
2. silicon carbide/graphite compound materials
3. carbon/graphite materials.

Altogether, 8 sliding ring materials are avialable for investigations (Tab. 2). Development work at several industrial companies as well as at KFA has contributed to this materials palette.

Identification of the phases in each material and determination of phase ratios have been performed by x-ray diffraction analysis and quantitative image analysis. The results are supported by investigation of the microstructure by use of ceramography and scanning electron microscopy.

Sliding ring seal	Material combinations for sliding rings		
	proposed and investigated for seals in the SNQ	used for seals in nuclear power stations	provided
with mixed friction	Si-SiC/Carbon(C*)	Si-SiC/Carbon(Sb*)	Si-SiC-C/Si-SiC-C
	Si-SiC-C/Carbon(C)	WC/Carbon(Sb)	
	Si-SiC-C/Si-SiC-C		
	Si-SiC/Si-SiC		
with dry friction	Si-SiC-C/Carbon(C)		
	Si-SiC-C/Carbon(Sb)		

* impregnation: carbon and antimony resp.

Tab. 1: Material combinations for sliding ring seals in the SNQ as well as in nuclear power stations

Material category		Material		
		Designation	Ratio of the main phases*	Density ($g \cdot cm^{-3}$)
1	Reaction-bonded SiC	Si-SiC	SiC : Si ≈ 8 : 1	3.07
2	SiC/graphite compound materials	Si-SiC-C	SiC : C_1 ≈ 1 : 1	2.87
			SiC : C_1 ≈ 2 : 1	2.65
			SiC : C_1 ≈ 4 : 1	2.90
3	Carbon/graphite materials	Carbon(C)	C_2 : C_1 ≈ 2 : 1	1.80
			C_2 : C_1 ≈ 3 : 1	1.65
			C_2 = 100%	1.50
		Carbon(Sb)	C_2 : C_1 ≈ 2 : 1	2.55

C_1 = carbon, predominantly ordered
C_2 = carbon, predominantly disordered
*ratio of the weight fractions (category 1 and 2)
ratio of the volume fractions (category 3)

Tab. 2: Sliding ring materials being investigated and irradiated for the SNQ seals

From the first material category, Si-SiC is available which has been already proved in industrial practice and sliding rings in large SNQ dimensions ($\emptyset \approx 400$ mm) have been successfully manufactured. Investigations show that the bearing part of the sliding ring material consisting of α / β-SiC amounts to about 85 vol.% with a ratio of α-phase to β-phase of about 7 : 1. β-SiC (cubic), due to the reaction of C and Si during silication, has been formed at the grain boundaries of α-SiC (hexagonal). The skeleton pores are filled with free Si.

From the 2nd material category three SiC/graphite compound materials are under investigation. They have been developed with regard to sliding rings and sliding bearings as well as for use as high temperature materials. They show high hardness and high resistance to wear as well as good chemical, thermal and thermal shock resistance. The main phases of the three materials are SiC and C_1 (predominantly ordered carbon, Tab. 2). Their ratios show a systematical variation. Additionally, different amounts of free Si are present. Till now, in most cases two phases were found in SiC. In the Si-SiC-C materials with ratios of SiC : $C_1 \approx 2 : 1$ and $\approx 4 : 1$ (coat-mix based material) (3) SiC mainly consists of the cubic -phase (95 %). Investigations of the first material have demonstrated that the structure is very homogeneous and consists of a matrix of SiC with embedded graphite grains. The free Si is evenly distributed. At present, sliding rings in SNQ dimensions consisting of SiC/graphite compound materials are not yet available. Development work at industrial companies is under way.

The main component of all the carbon/graphite materials belonging to the 3rd category, is predominantly disordered carbon (C_2). Especially with a view to dry friction three variants contain a portion of predominantly ordered carbon (C_1) for improving the self-lubricating properties. The coat-mix based material (4) with 100 % C_2 may be considered as a limiting case and is particularly suitable for obtaining a better understanding of the irradiation behaviour of the materials.

The carbon/graphite materials are divided according to their impregnation (carbon(C) and carbon(Sb)). C impregnation consists of binder coke (C_2) formed from resin during the coking process, this being the second C_2 component beside the filler coke. For impregnation of carbon(Sb), the metallic antimony is used. Both types of material distinctly differ from each other

in open porosity and surface roughness, which are higher for carbon (C); accordingly, the latter exhibits more space for water storage. Because of problems with carbon(Sb) used for seals with mixed friction in nuclear power stations (5), the carbon(C) variants seem to be more suitable for this seal type in the SNQ. Sliding rings of SNQ dimensions consisting of carbon(C) and carbon(Sb) are already available.

In order to establish complete data sets for the 8 sliding ring materials, extensive measurements for the determination of physical and mechanical properties are being performed. (2) In addition, special investigations concerning the material structure are under way.

Irradiation testing and first results

During SNQ operation, the sliding seals will be exposed to spallation neutrons. The expected operation conditions will be:

- time of operation: 12000 h
- max. operating temperature: for the seal with mixed friction 70°C, for that with dry friction 200°C
- max. accumulated spallation neutron fluences (in the case of ^{238}U as a target material): $1 \cdot 10^{19}$ and $1 \cdot 10^{20}$ cm^{-2} $E > 0{,}1$ MeV, respectively, for the two SNQ steps of development.

For the testing of sliding ring materials under conditions near those of SNQ operation, 2 experiments were performed in the spallation neutron environment at LAMPF. The test capsules were irradiated at different temperatures, thereby accumulating different fluences:

1st capsule: 60 - 100°C, $5.5 \cdot 10^{19} cm^{-2}$ E 0,1 MeV
2nd capsule: 120 - 150°C, $2.3 \cdot 10^{19} cm^{-2}$ E 0,1 MeV.

The capsules contained 20 and 19 samples machined from sliding rings of SNQ dimensions, representing the 3 different materials (categories 1 and 3):

- Si-SiC (SiC : Si 8 : 1)
- carbon(C) (C_2 : C_1 3 : 1)
- carbon(Sb) (C_2 : C_1 2 : 1)

First results for samples which allow a handling for measuring are summarized in Tab. 3.

Irradiation data	Material property/ Dimension	Irradiation-induced changes Si-SiC*	Carbon(C)**
spallation neutron - flux: ~$2 \cdot 10^{13} cm^{-2} s^{-1}$ E>0,1 MeV - fluence: ~$2.3 \cdot 10^{19} cm^{-2}$ E>0,1 MeV irradiation temperature: 120-150 °C	dimension	0 to + 0,04%	- 0,02 to + 0,03%
	density	within the limits of error	+ 3%
	thermal conductivity	- 51%	not determined
	Young's modulus	not determined	+ 66 % (II) + 148% (⊥)

*reaction-bonded SiC (SiC : Si = 8 : 1) **carbon/graphite material (C_2 : C_1 = 3 : 1)
Experiment SM-2

Tab. 3:
First results of irradiation testing of sliding ring materials in the spallation neutron environment at LAMPF

The materials Si-SiC and carbon(C) show very high dimensional stabilities and small changes in density. The thermal conductivity (k) of Si-SiC decreases significantly (- 51 %), in agreement with results for graphite irradiated in high flux reactors at low temperatures (6). The decrease can be correlated with the high scattering of phonons at irradiation-induced lattice defects at low irradiation temperatures. (7) Nevertheless, the reduced k-value of Si-SiC is in the range of the k-values of steels that are usually applied for structural parts surrounding the sliding ring seals. Measurements of the Young's modulus show high and anisotropic changes for carbon(C). This result is in agreement with results of fission reactor irradiations of other graphitic materials. (8) The high increase can be explained by the irradiation-induced pinning of mobile dislocations in the well-ordered regions and the reduced recombination probability of point defects at the low irradiation temperature. (9) As expected for the range of low temperatures, x-ray diffraction analyses showed no evidence for any irradiation-induced graphitization (10) of the predominantly disordered C_2 phase.

The results for carbon(C) are in good agreement with the results of carbon materials irradiated in the Dounreay Fast Reactor at 250°C up to a fluence of $1.8 \cdot 10^{20} cm^{-2}$ E 0.1 MeV. (11)

For irradiation testing of all the sliding materials (summarized in Tab. 2) another experiment at LAMPF is under way.

References

1) G. Bauer: ICANS-VII Symp., Chalk River, Ontario, Canada, Sept. 1983

2) W. Delle, R.-E. Schulze, M. Hofmann, K.H. Victor: Proc. Intern. Carbon Conf. Carbone 84, Bourdeaux, July 1984, 462-463

3) K. Bach, F.J. Dias, P. Glozbach, M. Kampel, K.H. Luhleich, P. Pflaum: Proc. Intern. Carbon Conf. Carbon 82, London, Sept. 1982, 16-18

4) F.J. Dias, K.H. Luhleich, H. Nickel, P. Pflaum: Proc. Intern. Carbon Conf. Carbon 82, London, Sept. 1982, 4-6

5) K.H. Walter: VGB Kraftwerkstechnik 63, 4, Aug. 1983

6) L. Binkele: J. Non-Equilib. Thermodyn. 3, 1978, 257-266

7) R. Taylor, B.T. Kelly, K.E. Gilchrist: J. Phys. and Chem. of Solids 30, 1969, 2251-2267

8) W. Delle, H.A. Schulze, R.-E. Schulze: Proc. 2nd Intern. Conf. on Structural Mechanics and Reactor Technology, Berlin, Sept. 1973, D 4/3

9) B.T. Kelly: Phil. Mag. 9, 1964, 721

10) W. Delle, G. Haag, H. Nickel, H.A. Schulze, R.-E. Schulze: Proc. 4th Intern. Conf. on Carbon and Graphite, London, Sept. 1974, 741-747

11) V.C. Howard, R.P. Thorne: J. Nucl. Mat. 16, 1965, 1965-172

Acknowledgement

The work described was carried out in the frame of the Project Spallation Neutron Source, SNQ (German: Spallation-Neutronenquelle) which is financed by the Federal Ministry of Research and Technology and the State of North-rhine-Westphalia.

RESULTS OF THE VISUAL IN-PILE INSPECTION OF THE INNER GRAPHITE REFLECTOR OF THE AVR

W. Delle *, N. Kirch*, H. Nickel*, E. Ziermann**

* Kernforschungsanlage Jülich GmbH, Postfach 1913, D-5170 Jülich
** Arbeitsgemeinschaft Versuchs-Reaktor GmbH, Stetternicher Forst, D-5170 Jülich

Introduction

Consideration is being given to reconstruct the high temperature gas-cooled pebble-bed reactor AVR for the application as a source of nuclear process heat. The reactor started in 1967 with a maximum gas outlet temperature of 750°C. Initially it was planned to operate the reactor for 10 years. After 8 years, it was decided to increase the maximum gas outlet temperature to 950°C to prove the possibility of generating gas temperatures which are relevant for nuclear process heat. Except for an interruption of about 1 year, the reactor was successfully operated until now with a maximum temperature of 950°C.

It is a basic requirement for a continuation of the research and development work with the AVR, that after about 16 years of operation, the main components of the reactor are in good condition so that they could be used for a further operation. One of the very important components is the inner graphite reflector. In the AVR, the upper side and the top reflectors were most exposed to fast neutrons and to the highest temperatures. By the end of 1984, the maximum fluences in the upper side reflector was 5×10^{21} cm^{-2} EDN at about 650°C and 1.2×10^{21} cm^{-2} EDN at temperatures at about 1000°C. (1)

To prove the integrity of the graphite reflector, it was decided to carry out a visual inspection of the upper reactor core.

Description of the equipment for visual inspection

The principle of the proceeding was as follows (fig. 1): A camera, especially developed for this purpose was led through the central charge tube. Because

of the small diameter (61 mm) and the small radius of the tube curvature (200 mm), the size of the camera had to be decreased to 155 mm in length and 35 mm in diameter. The full length of the way, on which the camera had to be moved through the tube into the core, was about 30 m (fig. 1). At the periphery of the reactor core, there are 4 more charge tubes which were used for the introduction of 4 spot-lights (fig. 2). The movements of the camera and of the spot-lights were remotely controlled. During inspection the spherical fuel elements had not to be removed from the core. By shutdown, the temperature was decreased to 50°C; the dose rate, which the equipment had to withstand, was 1.7×10^5 rad $\cdot$ h^{-1}. (2)

Reflector graphite

For the inner side and top reflector of the AVR, the needle coke graphite ARS/AMT produced by the Sigri Elektrographit Company was used. Parts of the side reflector and the graphite tubes for the control rods were extruded. The segments for the top reflector (fig. 3) were stamped. The properties of the ARS/AMT are comparable to those of the British PGA graphite which was manufactured by using the same raw materials (shell coke and pitch binder). A few samples of ARS/AMT were irradiated in the DRAGON reactor, in the High Flux Reactor in Petten and in the Dounreay Fast Reactor in the frame of the THTR Association during the sixties. Pre-production material was examined before and after irradiation in the General Electric Test Reactor in Vallecitos/Cal. (3)

The irradiation induced dimensional changes are in a range where the graphite is densified due to the decrease in the dimensions. In spite of a relative high anisotropy ($\alpha\perp / \alpha\parallel \approx 2$), the dimensional-changes take an comparatively isotropic course in the fluence and irradiation temperature range investigated. The densification was accompanied by an increase of Young's modulus and strength.

In the fluence region which the reflector has seen during the operation of the reactor, the coefficient of linear thermal expansion, CTE, increased at low fluence and then significantly decreased with dose, a well-known behaviour of polycrystalline graphite under fast neutron irradiation. Also thermal conductivity measured at room temperature decreased in the way known.

Results of visual inspection

The inner reflector of the AVR was photographically documented by the Hochtemperatur-Reaktorbau Company (HRB) before the reactor operation started. (4) By means of the camera, every block and segment were intensively considered several times. Special features, for example fracture of an edge or peculiar macro pore size distributions which had been photographed before reactor operation could be identified again and shapes as well as sizes were compared with the pre-irradiation values. The top and upper side reflectors appeared unchanged. Only the spaces between the segments of the top reflector which had a width of 2 mm in the original state appeared closed immediately at the core side. The inspection revealed that the closures had a very small depth so that is can be assumed that the disappearance of the spaces were due to filling with graphite powder. A further possibility is the movement of the segments due to thermal expansion and their changes under reactor operation. The segments were not fixed, but they were put on the side reflector (see fig. 2) so that a very small movement in the radial direction was possible..

The essential results of the visual inspection are that in spite of several shutdowns during 16 years of operation, no cracks or fractures were observed to have occurred. This is in agreement with the results obtained from the irradiation of small samples (fig. 4) as well as of stress calculations performed by HRB (5) and KFA (6).

Figures

References

1) Wolf, L.: Private communication, 1985

2) Delle, W., F. Krieger, P. Kulig, R. Polzenberg: Visuelle Inspektion des AVR-Decken- und oberen Seitenreflektors, Jahrestagung Kerntechnik, Munich, May 7-9, 1985

3) Delle, W., G. Pott, W. Brodmühler, A. Schmidt: Communication THTR 100, THTR Ass. Nr. 003-63-1 RGAD, 1972

4) Werkfoto HRB Mannheim

5) Schmidt, A.: Private communication, 1984

6) Hardtke, B.: Private communication, 1984

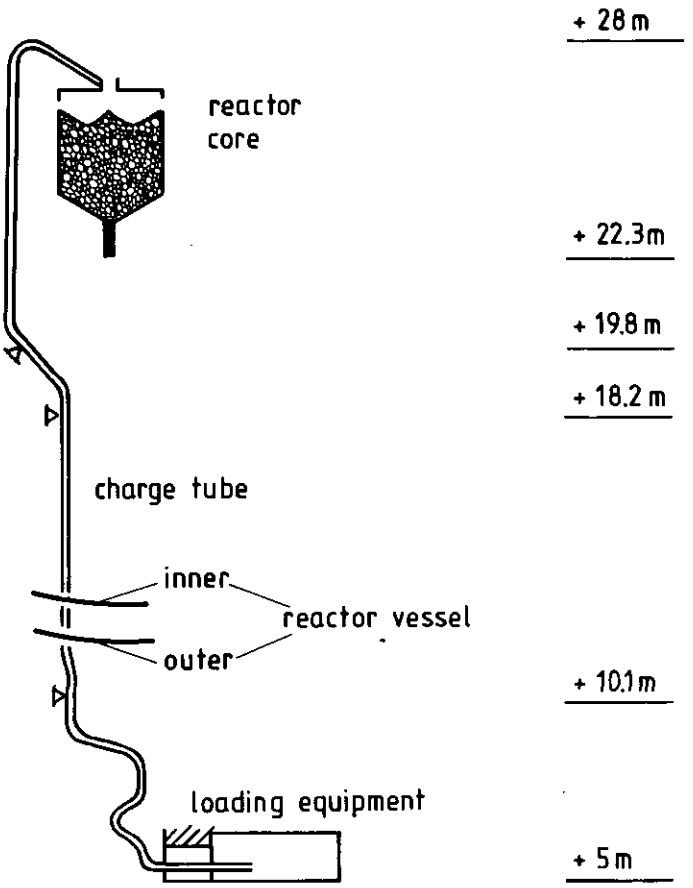


Fig. 1:
Schematic illustration of the central charge tube (2)

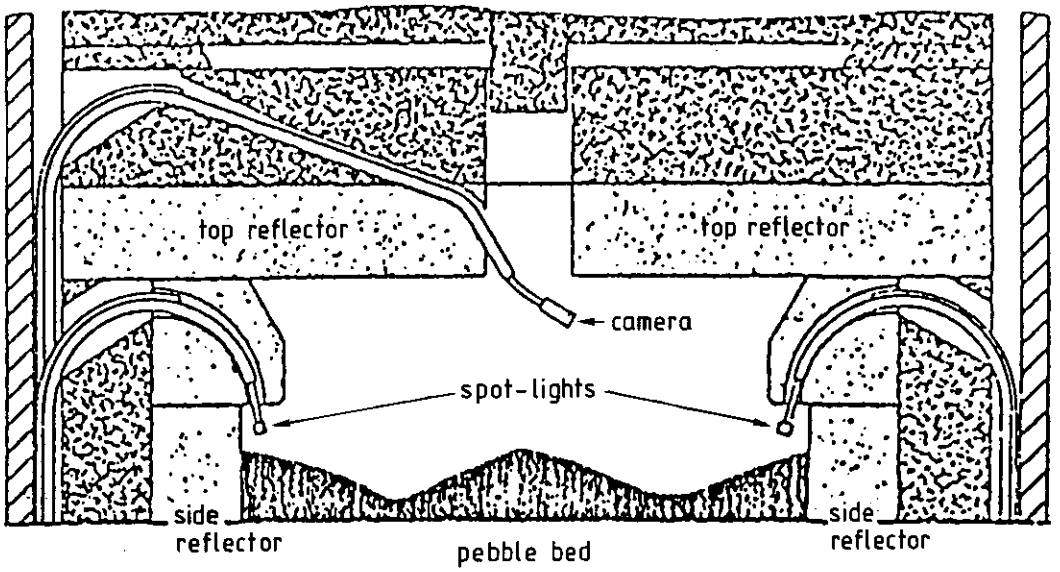


Fig. 2: Schematic illustration of the visual inspection (2)

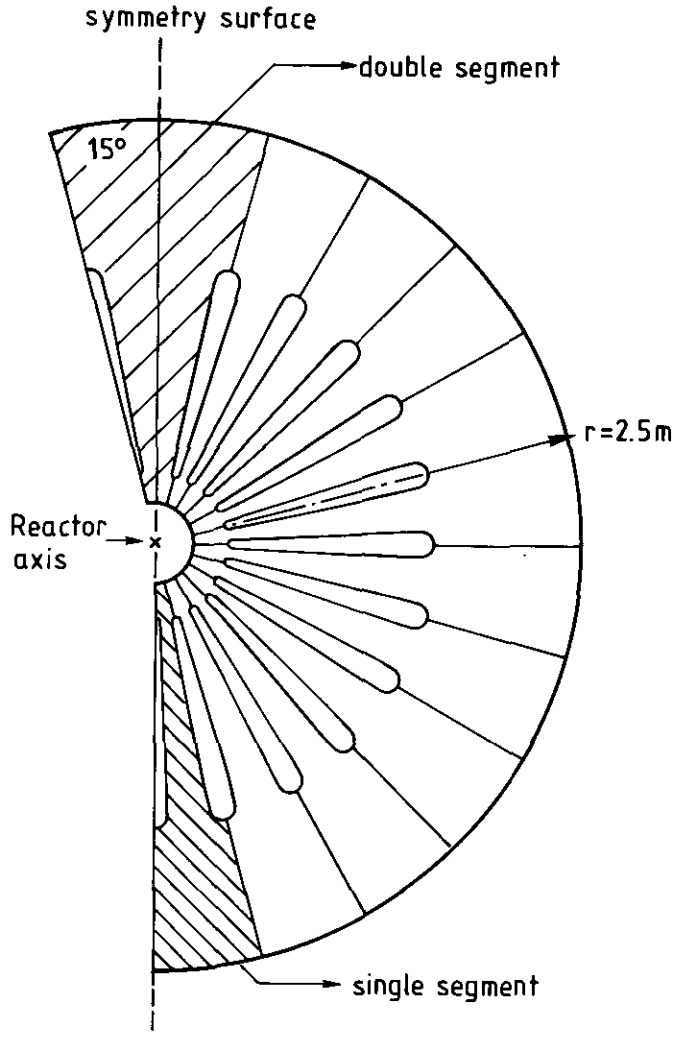


Fig. 3: Horizontal sectional view of the graphite top reflector (5)

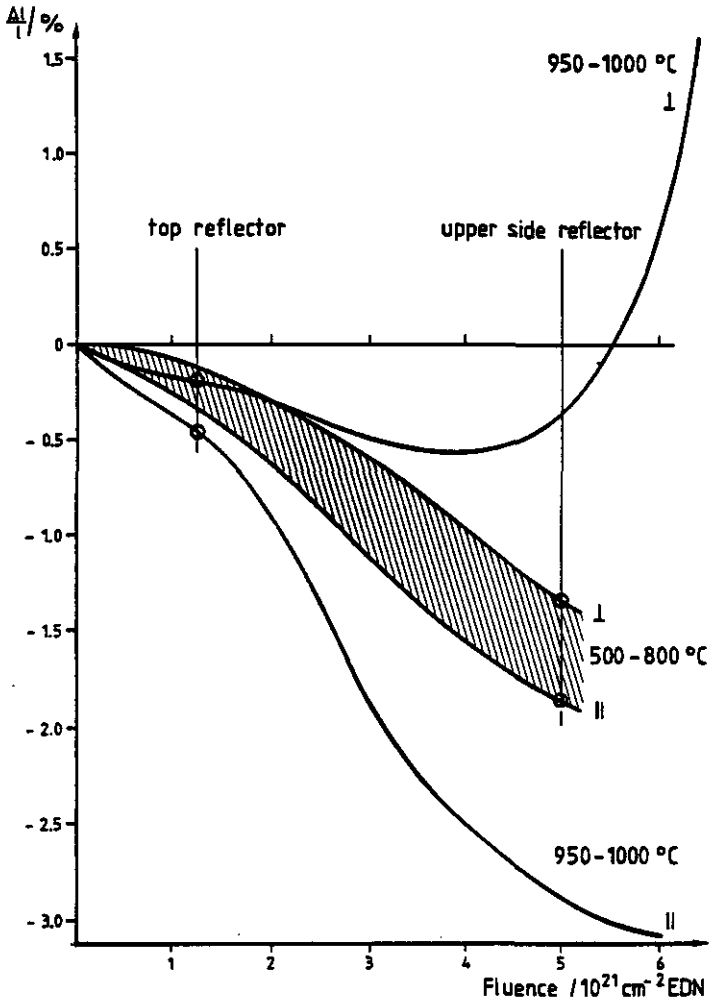


Fig. 4: Dimensional changes of ARS/AMT needle coke graphite with AVR conditions by the end of 1984

Acknowledgements

The visual inspection of the AVR was carried out in the frame of the project HTA (Hochtemperaturreaktor-Anlagen). The equipments for the visual inspection were designed and constructed as well as operated during the three days of examination by the Noell Company, Würzburg/FRG. AVR considerably supported the work which had to be carried out under difficult conditions.

The authors wish to thank Mr. K. Reinhart, Sigri GmbH who was one of the experts carried out the visual inspection. Because of his great experience in materials characterization, he contributed in a high extent to the opion on the state of the graphite reflector after operation.

WARM-MOULDED GRAPHITIC MATRIX FOR SPHERICAL HTR FUEL ELEMENTS

W. Delle, R.-E. Schulze, L. Binkele, G. Haag, W. Heit*, H.A. Schulze

Kernforschungsanlage Jülich GmbH, Postfach 1913, D-5170 Jülich
* Fa. HOBEG GmbH, Postfach 110029, D-6450 Hanau

1. Introduction

The development and irradiation testing of graphitic matrix materials for cold-moulded HTR fuel elements have been completed successfully with the use of two approved materials for the fuel elements of the reactors AVR (matrices A3-3 and A3-27) and THTR (matrix A3-3).

In order to enable the manufacture of fuel elements with high heavy-metal loading, as well as to improve the fabrication technology, the NUKEM/HOBEG company developed a process for the warm-moulding of the elements. (1) Furthermore, pitch coke graphite was used as a filler raw material instead of the mixture of natural graphite and petroleum coke graphite used before. On this basis, structural materials for warm-moulded fuel elements were developed and two optimized matrices (W2-1 and W2-2) were tested under fast neutron exposure at 700, 900 and 1100°C in the High Flux Reactor Petten, The Netherlands. Measurements of the sample dimensions and the physical properties were performed at KFA Jülich.

The present paper deals with some comparisons between the warm-moulded and the cold-moulded fuel matrices as far as the material composition, fabrication parameters, material properties and two of irradiation results are concerned.

2. Warm-moulded graphitic matrices compared to cold-moulded matrices

2.1 Material composition and fabrication parameters

Table 1 shows the compositions of the warm-moulded matrices W2-1 and W2-2 as well as those of the cold-moulded fuel matrices A3-3 and A3-27. The material W2-1 represents the standard quality of the first matrix category. Its variant W2-2 serves as a reference material and is especially intended to

provide a better understanding of irradiation behaviour. The materials differ only by their composition whereas the raw material and fabrication parameters are equal. The filler component consists of pitch coke graphite and the binder component has been made of phenolic resin binder to which 5 wt % of the hardener hexamethylenetetramine was added. As a moulding method, the warm-moulding in a steel die was used in contrast to the isostatic cold-moulding in rubber dies used before. Final heat treatment was carried out at 1950°C to achieve a favourable corrosion rate.

The two cold-moulded fuel matrices A3-3 and A3-27 are based on the same filler mixture consisting of natural graphite and petroleum coke graphite. They differ in the binder and its processing or synthesis. Whereas prefabricated phenolic resin binder is processed together with the filler components for fabricating the standard matrix A3-3, synthesis of the binder only takes place during the matrix formation for producing the material A3-27.

The two phenolic resin binders differ in binder type and crosslinking; consequently, the binder cokes are of different structures. (2) The process step of isostatic cold-moulding was the same for both materials. Final high-temperature treatment took place at different temperatures. Earlier fuel element reload batches for the AVR reactor, which had been produced with A3-3, as well as matrix spheres for machining irradiation specimens were subjected to a heat treatment at 1800°C. For later AVR reload batches and for the THTR production, the temperature was increased to 1950°C in order to improve the corrosion resistance.

Material		Filler	(wt%)	Binder	(wt%)	Hardener	*(wt%)	Binder coke (wt%)
Warm-moulded matrices	W2-1**	pitch coke graphite	84	phenol formaldehyde	16	hexamethylenetetramine	5	9.8
	W2-2		82		18		5	11.0
Cold-moulded matrices	A3-3	natural graphite + petroleum coke graphite	80		20	–	–	10.0
	A3-27		78	phenol*** hexamethylenetetramine	22	–	–	11.0

*related to the binder content **standard quality
***synthesized during matrix formation

Tab. 1:
Composition of warm-moulded and cold-moulded matrices

2.2 Material properties

In Table 2, material properties of the warm-moulded and the cold-moulded matrices are summarized. A comparison of the warm-moulded matrices W2-1 and W2-2 shows that the standard quality W2-1 exhibits a better strength behaviour than the matrix W2-2. Furthermore, the thermal conductivity determined at 1000°C and the Young's modulus are also somewhat more favourable for this material; only the higher corrosion rate points to a slightly more unfavourable corrosion behaviour. The coefficients of linear thermal expansion (α) determined between 20 and 500°C and, consequently, also their quotients $\alpha\perp/\alpha\parallel$ are similar for both materials. Comparing the material properties of the standard quality of the warm-moulded matrix (W2-1) with those of the cold-moulded fuel matrices A3-3 (1950°C), A3-3 (1800°C) and A3-27, the first shows a substantially better strength behaviour. On the other hand, the corrosion rate of W2-1 is more unfavourable than that of A3-3 (1950°C) and A3-27 (1950°C), although heat treated at the same temperature. (3) Moreover, moulding in a die, causes a higher quotient of thermal expansion coefficients ($\alpha\perp/\alpha\parallel$) for W2-1 and W2-2.

Material		High-temp. treatment	Application	Property											
				Young's modulus		Density	Coeff. of lin. therm. expansion 20-500 °C		Quotient of coeff. of therm. expansion	Therm. conductivity at 1000 °C		Compressive strength		Tensile strength		Corrosion rate at 1000 °C in He of 1 bar with 1 vol. % H_2O (10h)
		(°C)		(kN · cm^{-2}) ∥	⊥	(g · cm^{-3})	(10^{-6}K^{-1}) ∥	⊥	$\alpha_\perp/\alpha_\parallel$	(W · cm^{-1}K^{-1}) ∥	⊥	(daN · cm^{-2}) ∥	⊥	(daN · cm^{-2}) ∥	⊥	(mg·cm^{-2}h^{-1})
Warm-moulded matrices	W2-1	1950	Development of warm-moulded fuel elements	1095	882	1.73	2.94	3.73	1.27	0.30	0.27	844	832	225	200	1.14
	W2-2	1950		1110	980	1.74	2.97	3.70	1.25	0.28	0.26	775	740	132	164	1.01
Cold-moulded matrices	A3-3	1950	AVR fuel elements, THTR Production	1000	970	1.73	2.89	3.45	1.19	0.32	0.29	435	426	135	126	0.97
		1800	Previous AVR fuel elements	1020	991	1.70	2.80	2.92	1.07	0.28	0.27	382	376	104	105	1.19
	A3-27	1950	AVR fuel elements	1070	1020	1.74	2.43	2.69	1.11	0.34	0.32	469	464	135	130	0.73

* parallel and perpendicular to the equatorial plane of the matrix sphere ** standard quality

Tab. 2: Material properties of warm-moulded and cold-moulded matrices

2.3 Irradiation behaviour

In Figures 1 and 2 irradiation results concerning the dimensional behaviour and the thermal conductivity, resp. of the warm-moulded as well as the cold- moulded matrices are demonstrated.

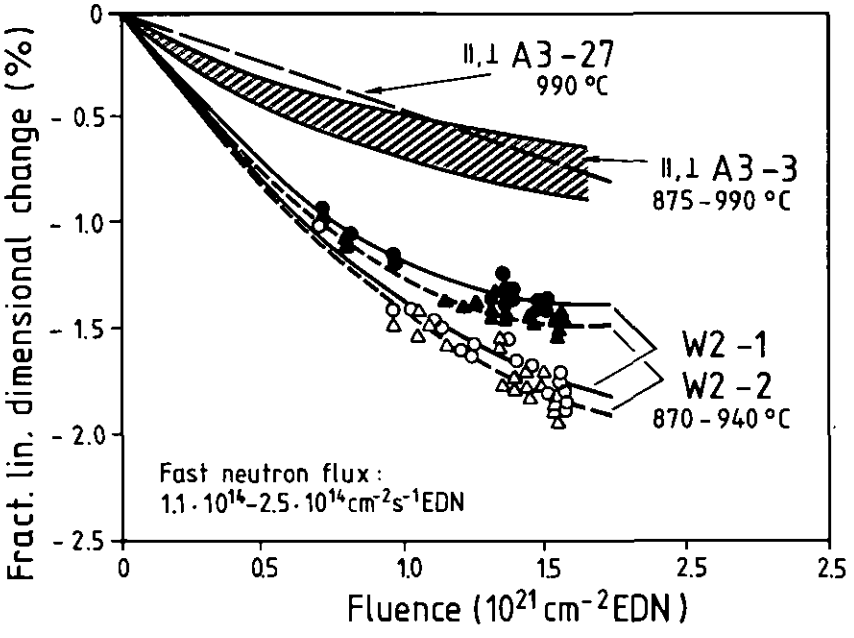


Fig. 1: Dimensional change of warm-moulded and cold-moulded matrices versus fluence

Fig. 1 shows higher dimensional changes versus fluence for both warm-moulded materials W2-1 and W2-2 compared to those of cold-moulded matrices A3-3 and A3-27. This different irradiation behaviour can be attributed to the different filler materials as well as to the differences in structure. (1,2) Furthermore W2-1 and W2-2 show slightly anisotropic dimensional behaviour analogous to their quotients of thermal expansion (Tab. 2), and they differ in skrinkage due to the different binder coke contents (Tab. 1). (4,5)

The thermal conductivity (k) of all four matrices generally decreases under irradiation, at temperatures of about 900°C approximating a saturation value of about 60 % of the pre-irradiation value (Fig. 2).

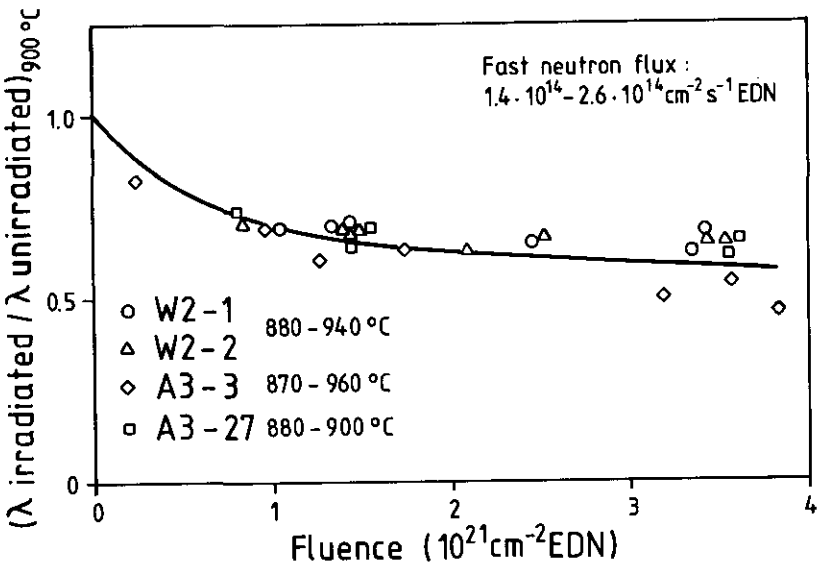


Fig. 2: Fractional change of thermal conductivity of warm-moulded and cold-moulded matrices versus versus fluence

3. References

1) R.-E. Schulze, H.A. Schulze, W. Rind: KFA report Jül-Spez.-167, July 1982

2) R.-E. Schulze, H.A. Schulze, W. Delle: Prepr. 5th Intern. Conf. on Carbon and Graphite, London, Sept. 1978, 904-917

3) W. Delle, B. Heinrich, W. Heit, A. Kleine-Tebbe, W. Rind, R.-E. Schulze: Prepr. Intern. Kohlenstofftagung, Carbon'76, Baden-Baden, June 1976, 357-360

4) W. Delle, G. Haag, H. Nickel, H.A. Schulze, R.-E. Schulze: Prepr. 4th Intern. Conf. on Industr. Carbon and Graphite, London, Sept. 1974, 741-747

5) R.-E. Schulze, W. Delle, L. Binkele, G. Haag, W. Rind, H.A. Schulze: Prepr. Intern. Carbon Conf. Carbone 84, Bordeaux, July 1984, 460-462

4. Acknowledgement

This work was carried out within the frame of the Project High Temperature Reactor Fuel Cycle, HBK (German: Hochtemperaturreaktor-Brennstoffkreislauf) which includes the partners GHT GmbH, HOBEG mbH, HRB GmbH, KFA Jülich GmbH, NUKEM GmbH and Sigri GmbH/Ringsdorff-Werke GmbH. It is financed by the Federal Ministry of Research and Technology and the State of Northrhine-Westphalia.